

Effect of PbO_2 on Co(III) generation and electrolyte emission performance analysis for sustainable use of electro-scrubbing process

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Abstract -- To enhance the oxidation of Co(II) by using PbO_2 anode and electrolyte emission test for sustainable utilization of electro-scrubbing process is the primary investigation. Introduction of PbO_2 electrode on oxidation effect of Co(II) demonstrated an enhanced oxidation efficiency to nearly 20% than Pt coated Ti electrode. The number concentration of the mists generated from the wet scrubber was an about 30 times lower than that of indoor air particles. No change in pH at second scrubber during 24 hr study explains no sulphuric acid escape from the first scrubber or mediated electrochemical solution. These results reveals that this electro-scrubber can maintain its initial concentration of Co(II) and H_2SO_4 by just adding water and thus becomes a highly sustainable system without losing of H_2SO_4 and Co catalysts to the environment.

Keywords: PbO_2 , sustainable, Mist particles, Electrocatalysts, electro scrubbing.

1. Introduction

Air pollutants removal through electro-scrubbing process is growing and environmentally friendly technology due to 'electron' has been used as catalysts. Some of air pollutants have been removed successfully by using electro-scrubbing process [1,2]. Though the process contains wider advantageous like removal can be done at room temperature and pressure, no excess catalyst is needed, smaller working area etc., some points should be considered for sustainable usage. Apart from electrode [3], membrane [4] stability for sustainable use, catalyst and electrolyte should be continuously generated and used respectively. First preventive measure in related with sustainable use of generated homogeneous catalyst in the electro-scrubbing process is the possibility of active catalyst migration to cathodic compartment and get reduced to inactive metal is crucial, which was prevented by simply modifying current supply mode [5]. Another possible measure to be prevented for sustainable operation of electro-scrubbing process is electrocatalyst and electrolytes should not be escaped from the electro-scrubbing process.

To our knowledge, no such measures were done in electro-scrubbing removal process. In this current investigation, electrolyte and catalyst loss is considered to develop sustainable use of electro-scrubbing process. Not only for sustainably operate the electro-scrubbing process, but to prove the electro-scrubbing process is one of a green methodology. Thus, to maintain its successful and complete sustainability, there should be no losses of electrolytic solutions by means of mists emission or liquid evaporation.

In order to increase more number of active electrocatalyst, various electrode materials have been attempted like Pt, Ti/Ir, and PbO_2 etc., [6-8]. Among many electrodes, BDD showed high current efficiency, but its cost expensive nature restricted to use in large industrial scale purposes. Next, Pt coated Titanium electrode evidenced considerable reduce in cost with moderate timing applications [9]. It is known widely that Pb is keep effectively serve as electrode in Pb-acid battery and comparatively cheaper than BDD. Also, PbO_2 demonstrated to showed high water splitting potential as of BDD [10] with high current efficiency. PbO_2 electrode has been considerably used in direct oxidation of water pollutants removal [11], Recently, one finding appeared use of $PbO_2/Sn_2O_3-SnO_2/Ti$ anode for oxidation of Ce(III) and its uses to acetaminophen oxidation [8]. It is proved previously from our group that oxidation of Ce(III) is totally contradictory with Co(II) especially temperature effect concerned on its oxidation [12,13]. In particular Co(II) oxidation was inversely proportional to temperature and no findings was reported on oxidation of Co(II) by PbO_2 .

In this proceedings, PbO_2 has been used as anode to increase the oxidation efficiency of Co(II) and compared with conventional Pt coated Ti electrode. Next, the losses of the scrubbing liquid (4 M H_2SO_4 + Co(III)) have been investigated by a variety of analysis such as mists number concentrations at the outlet of the scrubber, and pH changes of spraying water at the second scrubber downstream of the first scrubber.

2. Experimental

2.1 Materials

Cobalt sulfate ($Co(SO_4)_2 \cdot 7H_2O$, 99.9%) from TERIO Corporation, China, sulfuric acid (H_2SO_4 , 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) from Junsei Chemical Co., Ltd, Japan were used as received without any further purification. A Nafion® 324 membrane

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was purchased from DuPont, USA, and mesh-type Pt-coated-Ti and Ti plate electrodes were from Wesco, Korea. All the solutions were prepared using water purified by reverse osmosis (Human Power III plus, Korea). The air pollutants in cylinder H₂S (2% H₂S in N₂), NH₃ (10%), (CH₃)₃NH, CH₃CHO were supplied by P.S. Chem. Co., Ltd, Korea, and the oil free air compressor was supplied by Kyungwon Co., Korea.

2.2 Methods

The experimental set-up that used for the removal of air pollutants consisting of two main units: an electrochemical cell and a wet scrubber reactor column, as described elsewhere [9]. The electrochemical cell used for Co(III) generation that includes a plate-and-frame type narrow gap divided flow cell configuration, with a mesh type Pt-coated-Ti and PbO₂ anode and Ti cathode, separated by a Nafion 324 membrane. The PbO₂ electrode was synthesized in our lab by electrodeposition method [14]. The inter-electrode gap was maintained at 5 mm, with the help of two Viton rubber gaskets (thickness = 2 mm). The electrode assembly set-up was tightly clamped to Ti end plates using a filter press technique. Provisions were made with separate channel paths, by which the anolyte and catholyte solutions could flow to their respective electrodes. A 0.7 L solution of Cobalt (II) sulfate in 4 M sulfuric acid (enough protection was taken during preparation) and 0.5 L of 4 M sulfuric acid, taken into separate anolyte and catholyte glass tanks, respectively, were continuously circulated through the anode and cathode compartments of the electrochemical cell, at various constant flow rates (L min⁻¹), via a magnetic pump (Pan World Co., Ltd, Taiwan). The electrolysis for generation of the active Co(III) mediator was conducted galvanostatically by applying a constant current of 2.5 A or 3.5 A via a current source from Korea Switching Instrument. The effective surface area of each electrode exposed to the solution was 35 cm².

To investigate the emission of the mists, two wet scrubbers were used as shown in figure 1. First scrubber containing an electrolytic liquid of 4 M H₂SO₄ and 0.75 M Co(II) and second is an additional scrubber to remove the acid components may be generated at the first scrubber. Two scrubbers were made of Pyrex glass and had a column of an inner diameter of 50 mm and a height of 1 m. They were filled with rasching ring packings with a diameter of 10 mm and a height of 10 mm. The total height of the packings was about 80 mm. Clean compressed air with a controlled flow rate of 30 L/min by a mass flow controller (MFC) model (1179A13CS1BK-S, MKS Co. Ltd., USA) and electrolyte liquid with a liquid flow rate of 4 L /min were introduced by co-current flow pattern to the first scrubber until the volume of the electrolyte liquid reduced to about 3/4 of its initial volume. Similarly, desired concentration and flow rate of air pollutants were introduced to the first scrubber for their removal study. The size distribution of mist particles generated by the emission of the scrubbing liquid was measured using an

aerosol spectrometer (Model 1.109, GRIMM) at the outlet of the scrubber

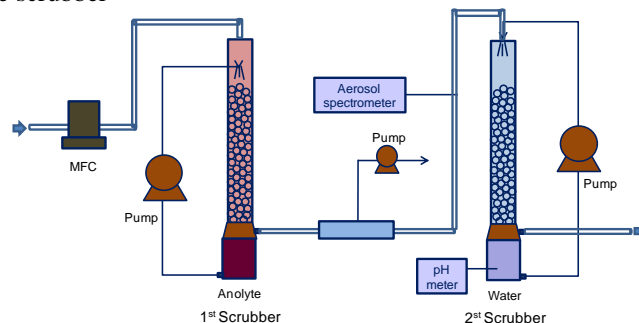


Fig. 1 Schematic representation of scrubbing unit for the mist emission tests

2.3 Analysis

The Co(II) to Co(III) oxidation conversion was assessed by measuring the Co(III) in the anolyte via a potentiometric titration with Fe(II) and oxidation reduction potential(ORP) measurements. The acidity change of the aqueous solution was measured at the second scrubber by using a pH meter (Model 220, Denver Instrument) during the mist emission tests. For removal efficiency analysis of air pollutants (NH₃, (CH₃)₃NH, CH₃CHO) were monitored online FTIR analyzer (model 1200-MIDAC Corp., Irvine, California) and H₂S was analyzed by GC/FPD (model GC-2010, Shimadzu, Japan) [1,9].

3. Result and Discussion

3.1 Effect of PbO₂ on Co(II) oxidation

Fig. 2 shows Co(II) oxidation effect with respect to time. The Co(II) oxidation on Pt electrode is increased from 0 to 60% at around 10 hrs, as shown in Fig.2(curve a). Also, the Co(II) and its formation of Co(III) is clearly depicted by their color at respective time interval as photo in Fig.2a. At the same time, Co(III) generation efficiency get increased when PbO₂ used as anode as shown in Fig. 2(curve b). There appears almost 19% more Co(III) was generated on PbO₂ than Pt/Ti, i.e., start from zero % and reached 79% in 5 hrs and keep maintained up to 8 hrs. It is clearly evidence the anode and water splitting potential are more influencing on electrogeneration of Co(III) [10]. The PbO₂ electrode was chosen for the further studies.



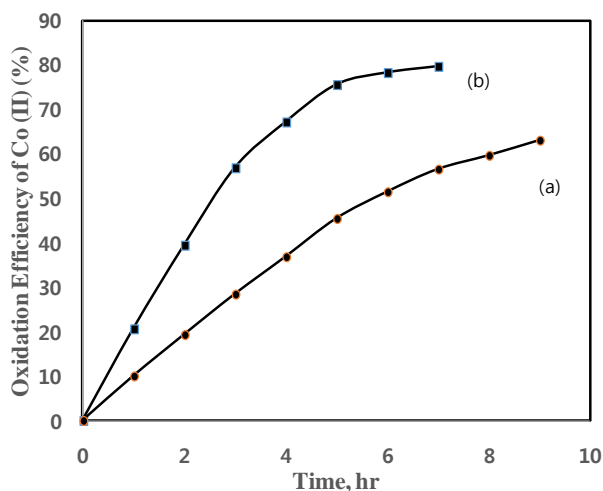


Fig.2 Comparative plot of Co(III) generation efficiency when used for different electrode (a) Pt coated Ti (b) PbO₂ with respect to time in 4 M H₂SO₄: Experimental conditions: Initial concentration of Co(II) = 0.75 M; liquid flow rate = 2 L min⁻¹.

3.2 Mist concentration at the outlet of the first scrubber

Figure 3(a) shows mist size distributions at the outlet of the first scrubber when using water, water with 0.75 M Co, and water with both 4 M H₂SO₄ and 0.75 M Co as scrubbing liquids. Mist particles were more or less generated in the order of 10⁶ m⁻³ with the sizes less than 3 μm for the scrubbing liquids containing 0.75 M Co or both 4 M H₂SO₄ and 0.75 M Co. However, the concentrations were about 30 times lower than those of indoor air particles of our laboratory (order of 10⁸ m⁻³) as shown in Fig. 3(b). This indicates that the mist emission at the outlet of the first scrubber is nearly negligible because the concentrations of diesel particles from vehicles or combustion particles from various industries were 10⁶ - 10⁷ times higher (i.e. order of 10¹² - 10¹³ m⁻³) than those of the mist particles [15,16].

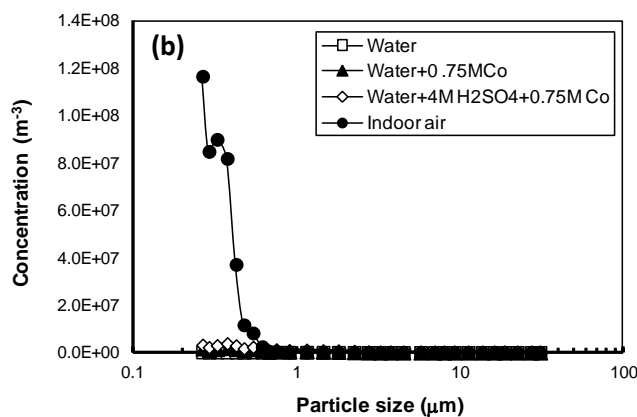
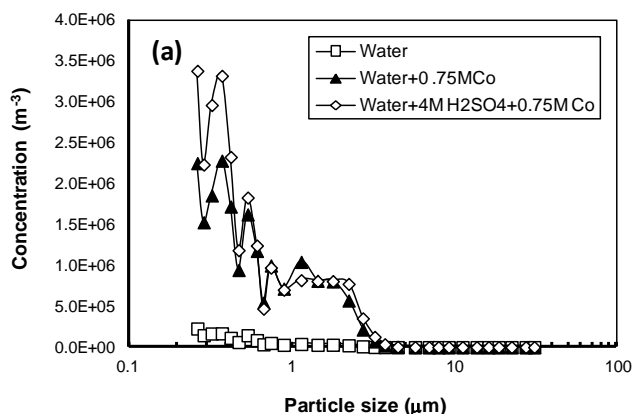


Fig. 3 (a) Mist concentration distributions with particle size for different solutions and (b) Mist concentration distribution comparison with indoor air particles concentration

3.3 pH analysis in water of the second scrubber

Figure 4 shows the pH changes of scrubbing solution in the second scrubber during the mist emission tests. For the first and second tests, NaOH was slightly added to the scrubbing water to make the initial pH be nearly 10 to remove easily acid components generated at the first scrubber. The pHs were reduced to about 7 after the emission tests and no further decreases were found. For the third test, pure water close to pH 7 was used as the scrubbing solution and pH was almost constant (pH ~ 7) during the emission test. This indicates that the most of lost components from the first scrubber was nearly pure water and it makes pH of the scrubbing liquid in the second scrubber be close to 7.

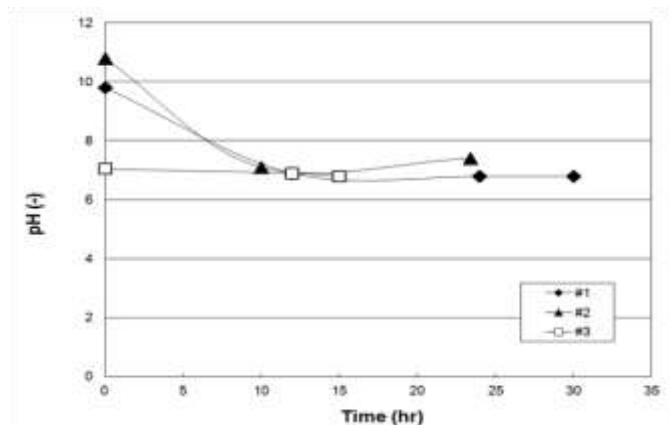


Fig. 4 Effect of pH changes in the scrubbing solution at the second scrubber with time.

3.4 Application to air pollutants removal

The removal of NH_3 , $(\text{CH}_3)_3\text{N}$, H_2S , and CH_3CHO air pollutants containing 100 ppm NH_3 , 100 ppm $(\text{CH}_3)_3\text{N}$, 10 ppm (H_2S) and 100 ppm CH_3CHO were studied at electro-scrubbing process. Removal profiles measured at the outlet of the scrubber reactor over time at 30 L min^{-1} is presented in Fig.5. At this gas flow rate (30 L min^{-1}), the electrogenerated Co^{III} in the scrubber reactor removed the air pollutants effectively at efficiencies approaching 100% (Fig.5) except H_2S . Removal efficiency of H_2S shows almost 95% in studied time. Co^{III} concentration variations in inset figure of Fig. 5, showed a slight increase with time, meaning that the Co^{III} regeneration rate faster than input air pollutant's concentration.

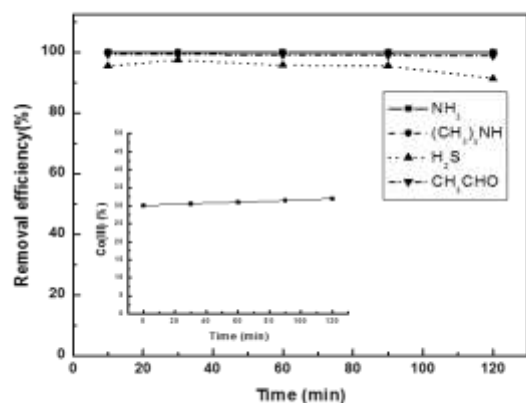


Fig. 5 Air pollutants removal efficiency as a function of time. Feed concentration of H_2S (10 ppm); NH_3 (100 ppm); $(\text{CH}_3)_3\text{NH}$ (100 ppm); CH_3CHO (100 ppm); Initial concentration of $\text{Co}(\text{II}) = 0.75 \text{ M}$; Gas flow rate = 30 L min^{-1} Liquid flow rate = 2 L min^{-1} . Inset shows the $\text{Co}(\text{III})$ concentration effect with time during air pollutants removal.

4. Conclusions

We successfully introduced PbO_2 as anode to enhance the $\text{Co}(\text{II})$ oxidation efficiency and investigated the mist emission tests how much losses of electrolyte and $\text{Co}(\text{III})/(\text{II})$ catalyst from the scrubbing liquid exit through the outlet of the scrubber. Upon using PbO_2 electrode, nearly 20% $\text{Co}(\text{III})$ was generated more, which will facilitate the removal of pollutants. Mist particles emitted at the outlet of the scrubber were negligible compared to indoor air particles. These results evidences most of the evaporated liquid from the scrubber is almost water, which means the electro-scrubbing process is green methodology. Further, initial concentration of the scrubbing liquid can be easily recovered by adding some water to it. Therefore, it has been proved by this study that the electro-scrubbing technology using homogeneous mediated electrochemical oxidation process is a highly sustainable process.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) funded by the Korea government (MEST) (Grant No. 2010-0027330) and the Eco Innovation Project of the Ministry of Environment (KEITI), Republic of Korea (Grant No. 411-111-010).

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